Borinine (Borabenzene): Its Structure and Vibrational Spectrum. A Quantumchemical Study

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Recently we reported the results of some semiempirical and *ab initio* studies in which we compared the electronic structure of the hitherto unknown borinine with those of benzene and pyridine. The results of our calculations led us to the conclusion that the elusive nature of borabenzene is caused by its high reactivity, which might at least in part be due to the pronounced σ acceptor properties of a low-lying σ^* molecular orbital.

We now present the results of further *ab initio* and semiempirical (MNDO) investigations in which we performed full geometry optimizations for the molecule using two different basis sets (STO-3G, 4-31G) and also calculated the vibrational spectra of the ^{10}B and ^{11}B isotopomeric borabenzene molecules at the 4-31G level of *ab initio* theory and with the semiempirical MNDO method.

The calculated vibrational spectrum might be helpful to the experimentalist in identifying the molecule, for example trapped in a rare gas matrix among the side products.

The calculated orbital energies can be useful in identifying the molecule by means of its photoelectron spectrum.

1. Introduction

Although a lot of borabenzene complexes are known [1], and even though it was possible to trap the molecule with pyridine [2, 3] to our knowledge no preparation and characterization of the unsubstituted neutral borinine* has been reported until today. The problems which obviously occur during the preparation of this elusive molecule may have two reasons:

1. In contrast to the substituted borinine derivatives, which serve as ligands in the complexes mentioned above, and different from the situation in its trapping product with pyridine, the unsubstituted and unstabilized sixmembered ring might be no longer a minimum on the C_5H_5B hypersurface.
2. The high reactivity of the target molecule is the reason for its elusive character.

In a previous study [4] we found that at least at the semiempirical MNDO level the C_{2v} hexagon is a stationary point on the C_5H_5B hypersurface. Further it was found, that among its doubly occupied orbitals there are three of π symmetry. This last result was confirmed by an STO-3G single point calculation using the MNDO optimized structure [4]. If we accept three doubly occupied molecular orbitals of π symmetry in a planar perimeter as a criterion for aromaticity, we have to consider the closed shell singlet of borinine as an aromatic. This aromatic however, in contrast with e.g. pyridine and phosphabenzene, should be destabilized by its pronounced acceptor properties, which are due to a low-lying σ^* orbital [4]. The reason for the hitherto fruitless attempts to prepare and characterize the borabenzene molecule [3] may therefore lie in its high reactivity which might cause reactions even with relatively inert matrix and carrier gases, not to speak of those possible reactions with molecules of reactants and of side products.

The results of our preceeding study are further supported by the calculations presented here, which not only prove that the planar sixmembered ring of C_{2v} symmetry is a real minimum at the MNDO level, but that similar minima exist at the STO-3G and 4-31G level of *ab initio* theory, too.

The identification of the molecule, for example trapped in a matrix, will be facilitated if one knows something about its spectroscopic properties in

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* For nomenclature see [1].

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advance. We therefore calculated the vibrational spectra of both isotopomers, containing either ^{10}B or ^{11}B atoms. These calculations were performed using a 4-31 G basis set [5], as well as the semi-empirical MNDO method [6].

2. Computational method

All calculations were performed on the CDC Cyber 175 of the Rechenzentrum der RWTH Aachen. For the *ab initio* calculations we used the HONDO5 program package [7]. Geometry optimization at the STO-3G level [8] was started from a planar hexagon with the following bond distances and angles* (for numbering of atoms see Figure 1): B_1-C_2: 1.53 Å, C_2-C_3: 1.40 Å, C_3-C_4: 1.41 Å, C−H: 1.10 Å, $\sphericalangle C_2-B_1-C_6$: 113.8°, $\sphericalangle B_1-C_2-C_3$: 119.8°, $\sphericalangle C_2-C_3-C_4$: 124.9°, $\sphericalangle C_3-C_4-C_5$: 116.8°, $\sphericalangle B_1-C_2-H$: 121.1°, $\sphericalangle C_2-C_3-H$: 118.4°. The STO-3G optimized structure was then used as a starting point for optimization at the 4-31G level [5]. If not mentioned otherwise, no symmetry constraints have been imposed during the optimization procedure. However, symmetry constraints turned out to be indispensable in the calculation of the vibrational spectra. Otherwise, the HONDO5 program did not "recognize" the symmetry of the molecule.

The natural abundances of the two stable boron isotopes are 80.22% ^{11}B and 19.78% ^{10}B [10], leading to an average atomic mass of 10.811. Due to the high percentage of ^{10}B, the vibrational spectrum of $C_5H_5{}^{10}B$ should be observed beside that of $C_5H_5{}^{11}B$ in a sample containing borabenzene, prepared from precursors containing boron in its natural isotopic composition. Because the electronic structures, and therefore the force constant matrices of isotopic molecules are the same to a high level of approximation [11], we calculated the isotopic shifts by massweighting the cartesian force constant matrix once using 10 and once 11 for the atomic mass of boron.

In the HONDO5 program the force constant matrix was calculated by the force method [12], in which the calculation of the second derivatives is accomplished by numerical differentiation of analytical gradients [13]. In the case of the semi-empirical method, this matrix was calculated completely numerically, using a standard MNDO program [14], modified by us. In the calculation of the second derivatives we used a step width of 0.01 Å.

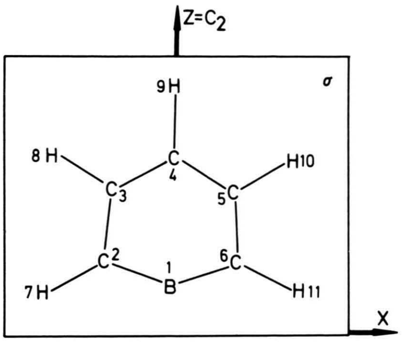

Fig. 1. Choice of coordinate system in symmetry analysis of the vibrational spectra and the molecular orbitals.

3. Results and Discussion

The total energies of the optimized structures are given in Table 1. To get an idea of the quality of the MNDO optimized geometry, the total energies of the MNDO structure at the STO-3G (STO-3G/MNDO)* and the 4-31G level (4-31G/MNDO) are listed there, too. In addition Table 1 contains the 4-31G energy of the STO-3G optimized structure (4-31G/STO-3G).

The structures of the molecule optimized at the different levels of theory employed here are shown in Figure 2**. With all methods the molecule turned out to be planar. Checking the eigenvalues of the force constant matrices confirmed that all structures are true minima.

Alternation of the bond lengths in the ring is only weak. According to both *ab initio* methods the bond lengths decrease in the order $B_1-C_2 > C_2-C_3 > C_3-C_4$, whereas MNDO gives the order $B_1-C_2 = C_3-C_4 < C_2-C_3$. Different

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* Bond lengths and the angle at boron were taken from the boratabenzene part of the ligand in tricarbonyl(1-phenylborinato)manganese [9].

* The symbol (method 2/method 1) means that the geometry has been optimized with method 1, while a single point calculation using that structure has been performed with method 2.

** Our STO-3G minimum is completely different from the one given in [15].

Table 1. Total energies (in a. u.).

Method	Total energy
STO-3G/MNDO	−214.197667
4-31G/MNDO	−216.554189
STO-3G/STO-3G	−214.200641
4-31G/STO-3G	−216.557482
4-31G/4-31G	−216.558625

Table 2a. Eigenvalues of the borinine molecule according to STO-3G/STO-3G (all values in a. u.).

No.	ε	Type
21	0.23616	$11\,a_1(\sigma)$ LUMO
20	−0.23696	$2\,b_2(\pi)$ HOMO
19	−0.27888	$1\,a_2(\pi)$
18	−0.41753	$7\,b_1$
17	−0.44064	$1\,b_2(\pi)$
16	−0.45171	$10\,a_1$
15	−0.51069	$6\,b_1$
14	−0.51664	$9\,a_1$
13	−0.55312	$5\,b_1$
12	−0.63016	$8\,a_1$
11	−0.68037	$7\,a_1$
10	−0.74689	$4\,b_1$
9	−0.87105	$6\,a_1$
8	−0.95361	$3\,b_1$
7	−1.06011	$5\,a_1$
6	−7.39108	$4\,a_1$
5	−10.98787	$2\,b_1$
4	−10.98793	$3\,a_1$
3	−10.99609	$2\,a_1$
2	−11.03136	$1\,a_1$
1	−11.03140	$1\,b_1$

Table 2b. Eigenvalues of the borinine molecule according to 4-31G/4-31G (all values in a. u.).

No.	ε	Type
21	0.10219	$11\,a_1(\sigma)$ LUMO
20	−0.29264	$2\,b_2(\pi)$ HOMO
19	−0.33634	$1\,a_2(\pi)$
18	−0.47559	$7\,b_1$
17	−0.48314	$1\,b_2(\pi)$
16	−0.50792	$10\,a_1$
15	−0.57198	$9\,a_1$
14	−0.57391	$6\,b_1$
13	−0.60707	$5\,b_1$
12	−0.67986	$8\,a_1$
11	−0.73408	$7\,a_1$
10	−0.80390	$4\,b_1$
9	−0.93039	$6\,a_1$
8	−1.01324	$3\,b_1$
7	−1.11995	$5\,a_1$
6	−7.60082	$4\,a_1$
5	−11.18998	$2\,b_1$
4	−11.19002	$3\,a_1$
3	−11.19138	$2\,a_1$
2	−11.22433	$1\,a_1$
1	−11.22436	$1\,b_1$

from the case of pyridine [16] some of the bond angles significantly deviate from 120°. Common feature of the optimized structures is, beside their planarity, the wide $C_2-B_1-C_6$ angle. MNDO clearly overestimates this angle. The value calculated by this method is 3.9 or 5.5 degrees higher than the corresponding STO-3G or 4-31G value, respectively. In spite of the somewhat too large $C_2-B_1-C_6$ angle, the MNDO optimized structure seems to be a fair approximation: Use of this structure in STO-3G and 4-31G single point HF-SCF calculations yields more than 99.99% of the total energies calculated for the corresponding *ab initio* minima. Comparing the STO-3G and 4-31G optimized structures, the largest difference between the results of both methods is found for the $C_2-B_1-C_6$ angle. The value of the STO-3G optimized structure is about 1.6 degrees larger than the angle found employing the 4-31G basis set.

While the STO-3G/STO-3G total energy is still 2.36 a.u. higher than the 4-31G/4-31G value, a 4-31G/STO-3G calculation yields a total energy, which lies only 0.0011 a. u. above the corresponding

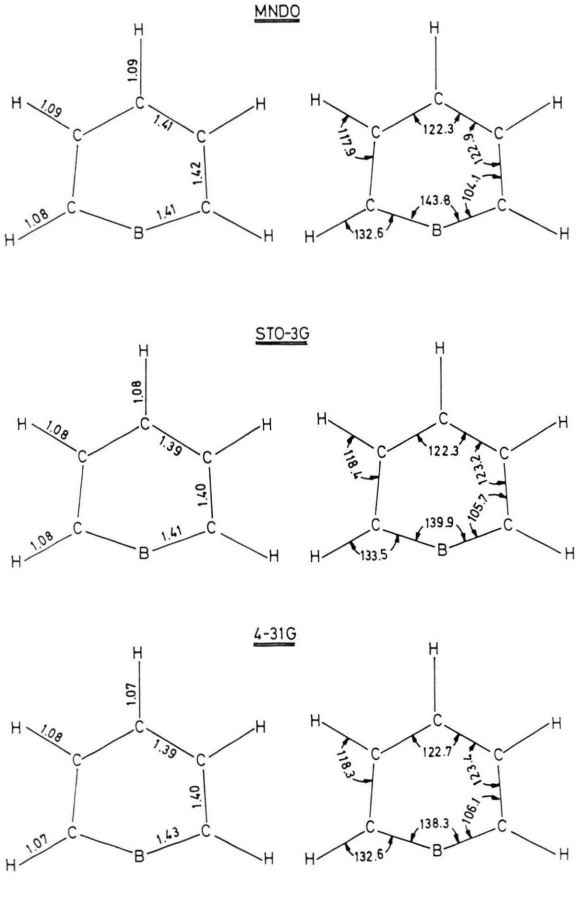

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Fig. 2. Bond lengths and bond angles in borinine according to 4-31G/4-31G, STO-3G/STO-3G, and MNDO [4]. Bondlengths in Å, angles in degrees.

Table 3. Energy difference between the two highest occupied molecular orbitals of π symmetry in some hetero aromatics (all values in eV).

Molecule	STO-3G/ STO-3G	4-31G/4-31G	MNDO
Borinine	1.14	1.19	0.51
Pyridine	0.53	0.79	0.83
Silabenzene [13]	2.12	—	—

4-31G/4-31G result. Consequently, extending the basis set from STO-3G to 4-31G quality mainly leads to a drop of the total energy, while the changes in geometry are of minor importance.

The energies of the occupied molecular orbitals and the LUMO, together with their symmetries, are listed in Table 2a and Table 2b.

In agreement with our earlier results both *ab initio* methods give three doubly occupied molecular orbitals of π symmetry, which include the HOMO ($2b_2$) and the level just below ($1a_2$). The LUMO, being of σ symmetry ($11a_1$), has its largest coefficients at the boron atom, corresponding to the low-lying σ^* acceptor orbital, which might at least in part be responsible for the assumed high reactivity of borinine. Except for the $9a_1$ and the $6b_1$ orbitals which are very similar in energy the order of the occupied levels is the same according to STO-3G/STO-3G and 4-31G/4-31G.

At both *ab initio* levels the perturbation of the typical benzoid orbital pattern is stronger than in the case of pyridine (cf. Table 3). With 1.14 eV and 1.19 eV for borinine the STO-3G/STO-3G and 4-31G/4-31G values for the energy gap between the two highest filled molecular orbitals of π symmetry are 0.61 and 0.40 eV higher than for pyridine (STO-3G/STO-3G: 0.53 eV; 4-31G/4-31G: 0.79 eV). However, these values are still smaller than in the case of silabenzene, for which a STO-3G value of 2.12 eV has been reported [17].

The calculated energy of the HOMO might be useful for the experimentalist in identifying the borinine molecule among pyrolysis or photolysis products in a photoelectron spectrometer by means of its first vertical ionization potential. The 4-31G/4-31G result predicts a value of 7.96 eV for the first vertical ionization potential, whereas STO-3G/STO-3G gives a significantly lower value of 6.45 eV and MNDO a somewhat higher one of 8.86 eV (cf. Table 4). With 8.03 eV and 8.02 eV the 4-31G/MNDO and 4-31G/STO-3G values are rather close to the value gained at the highest level of theory employed here.

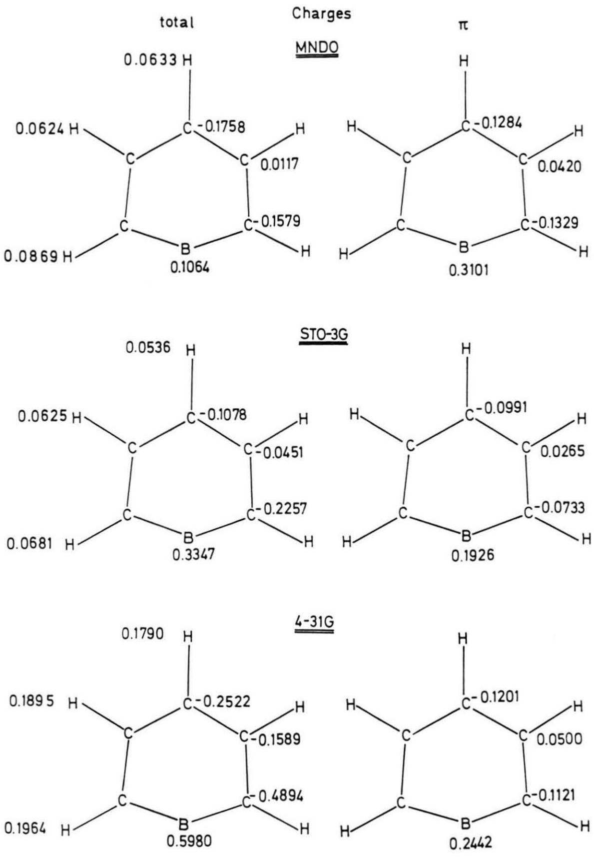

Fig. 3. Mulliken total and π charges in borinine according to 4-31G/4-31G, STO-3G/STO-3G, and MNDO [4]. All values in e_0.

Mulliken's total and π charges for borinine are plotted in Figure 3. Both *ab initio* methods give positive total charges at the boron atom, whereas the other atoms of the ring are charged negatively. The σ as well as the π system of the molecule is polarized considerably. MNDO and *ab initio* data however contradict each other in one important respect: Whereas according to the nonempirical calculations boron carries a positive π and σ charge, MNDO gives a negative value ($-0.20\,e_0$) for the latter. Different from the *ab initio* methods MNDO gives positively charged meta carbon atoms.

The dipole moments calculated are listed in Table 5.

Table 4. First vertical ionization potentials according to Koopmans' theorem (in eV).

Method	Value
MNDO	8.86
STO-3G/MNDO	6.42
4-31G/MNDO	8.03
STO-3G/STO-3G	6.45
4-31G/STO-3G	8.02
4-31G/4-31G	7.96

Table 5. Dipole moments in D.

Method	Value
MNDO	0.42
STO-3G/MNDO	0.91
4-31G/MNDO	0.73
STO-3G/STO-3G	1.03
4-31G/STO-3G	0.80
4-31G/4-31G	0.85

Table 6a. 4-31G/4-31G vibrational frequencies (all values in cm^{-1}).

$C_5H_5{}^{11}B$	$C_5H_5{}^{10}B$
A_1	
3397.3(2)	3397.4(2)
3342.3(3)	3342.3(3)
3301.9(5)	3301.9(5)
1674.9(7)	1674.9(7)
1516.7(9)	1518.9(9)
1281.1(12)	1281.5(12)
1054.2(17)	1055.6(17)
1042.1(18)	1042.1(18)
970.6(20)	986.0(19)
638.8(24)	653.1(24)
A_2	
1132.4(15)	1132.4(15)
859.8(21)	859.8(21)
465.1(26)	465.1(26)
B_1	
3398.0(1)	3398.1(1)
3308.6(4)	3308.6(4)
1749.3(6)	1776.0(6)
1608.6(8)	1613.5(8)
1428.0(10)	1444.8(10)
1311.9(11)	1312.1(11)
1268.7(13)	1272.3(13)
1129.4(16)	1129.6(16)
563.1(25)	564.9(25)
B_2	
1159.9(14)	1159.9(14)
980.9(19)	981.4(20)
814.1(22)	816.1(22)
708.9(23)	711.6(23)
430.0(27)	439.9(27)

Table 6b. MNDO vibrational frequencies (all values in cm^{-1}).

$C_5H_5{}^{11}B$	$C_5H_5{}^{10}B$
A_1	
3466.5(2)	3466.5(2)
3416.3(3)	3416.3(3)
3395.1(5)	3395.1(5)
1628.8(7)	1628.8(7)
1395.1(9)	1396.9(9)
1206.4(12)	1208.2(12)
1167.3(13)	1171.6(13)
1016.2(17)	1017.2(17)
870.1(20)	881.7(20)
593.0(23)	605.1(23)
A_2	
1006.8(18)	1006.8(18)
829.4(21)	829.4(21)
364.9(26)	364.9(26)
B_1	
3467.1(1)	3467.1(1)
3398.0(4)	3398.0(4)
1749.6(6)	1786.4(6)
1530.3(8)	1533.6(8)
1306.5(10)	1310.3(10)
1272.8(11)	1274.5(11)
1123.9(14)	1125.5(14)
1081.0(15)	1085.2(15)
479.5(25)	481.4(25)
B_2	
1040.9(16)	1040.9(16)
927.8(19)	928.6(19)
762.8(22)	764.0(22)
522.4(24)	524.3(24)
350.0(27)	359.3(27)

The vibrational spectrum of the borabenzene molecule was calculated at the 4-31G/4-31G level and compared with the corresponding MNDO result. Neither use of the still rather small 4-31G basis set, nor application of the semiempirical MNDO method is expected to reproduce the vibrational spectrum numerically. So, for example, the vibrational frequencies calculated at the 4-31G level usually are too high. However, at least at the *ab initio* level, the patterns of the calculated and the measured spectra are supposed to coincide qualitatively as it is known from other cases [18]*.

Six eigenvalues of the mass-weighted force constant matrices were found to be close to zero, corresponding to the three translations and rotations ("non genuine normal vibrations") of the molecule. For borabenzene one expects ten genuine normal vibrations of A_1, three of A_2 (which are active in Raman only), five of B_2, and nine of B_1 symmetry. Within the coordinate system chosen (see Figure 1) the vibrations lying in the plane of the molecule transform like A_1 or B_1, whereas the out-of-plane vibrations transform like A_2 or B_2.

The calculated vibrational frequencies are listed in Table 6a (4-31G/4-31G), and Table 6b (MNDO). The cartesian displacement vectors from the 4-31G/4-31G analysis are plotted in Figures 4a–4d.

The line spectra are shown in Figure 5a (4-31G/4-31G) and Figure 5b (MNDO).

Those normal vibrations which are located predominantly in the C–H regions of the molecule absorb between 3400 and 3300 cm^{-1} and form a block which is clearly separated from the rest of the spectrum by about 1550 wavenumbers*. Vibra-

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* For pyridine, e.g., see [16].

* If not mentioned otherwise, the spectrum calculated at the 4-31G/4-31G level is discussed.

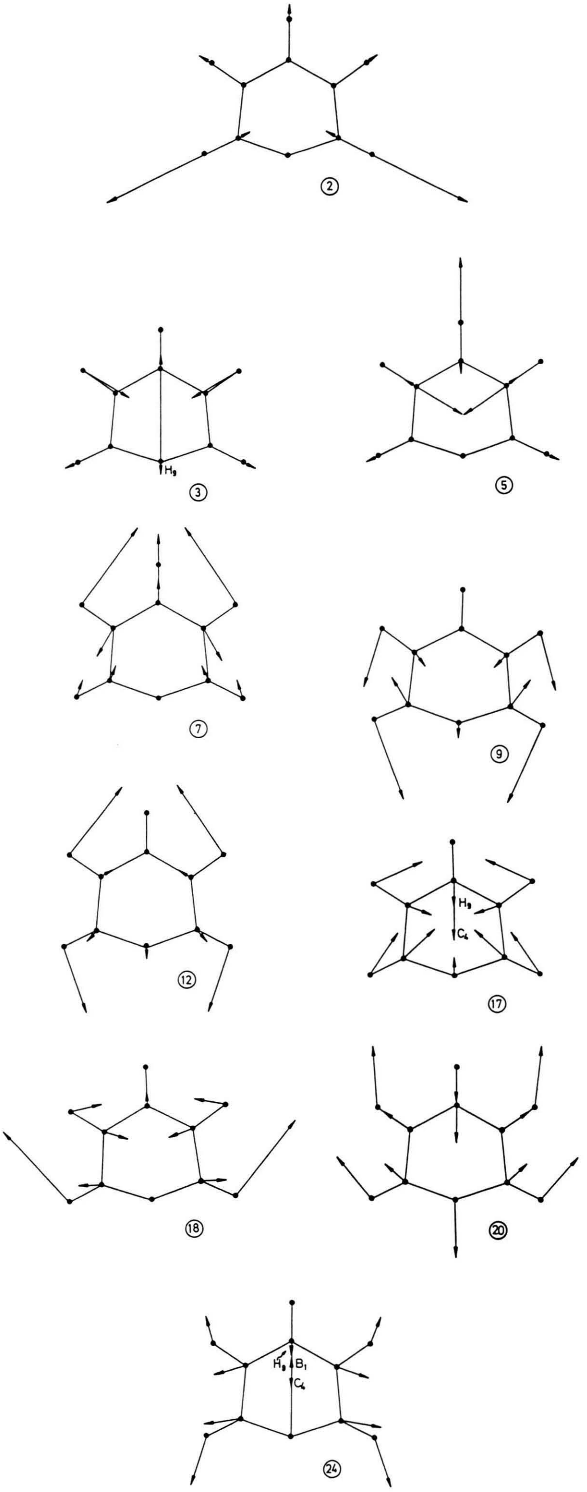


Fig. 4a. Cartesian displacement vectors (4-31G/4-31G) of A_1 symmetry (^{11}B). For frequencies see Table 6a.

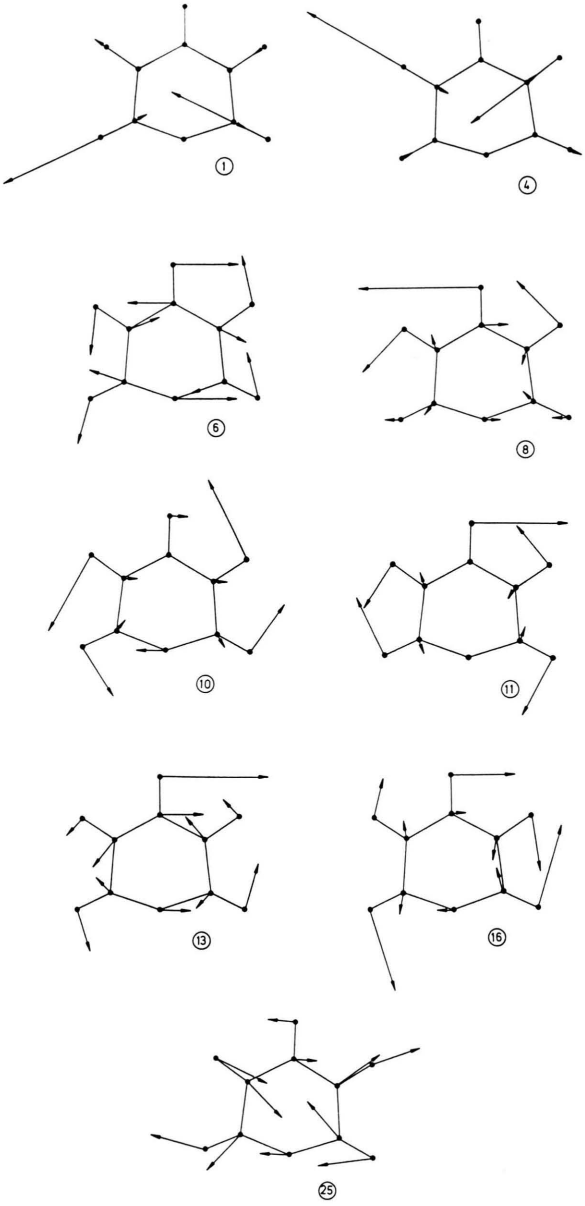


Fig. 4b. Cartesian displacement vectors (4-31G/4-31G) of B_1 symmetry (^{11}B). For frequencies see Table 6a.

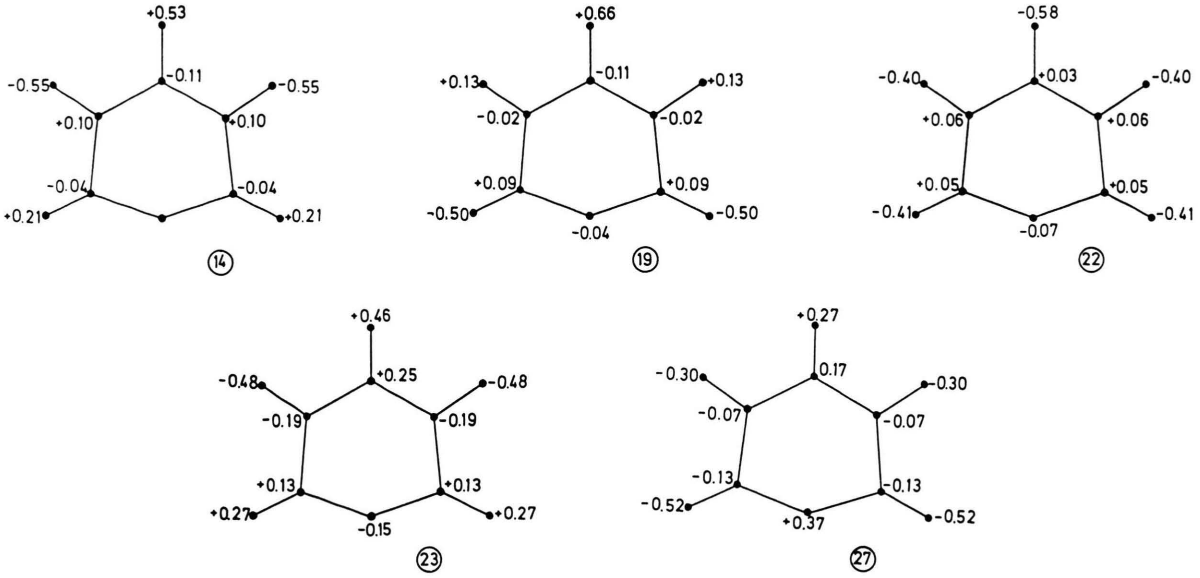


Fig. 4c. Cartesian displacement vectors (4-31G/4-31G) of B_2 symmetry (^{11}B). The numbers at the atoms correspond to the values of the y-components (cf. Figure 1). For frequencies see Table 6a.

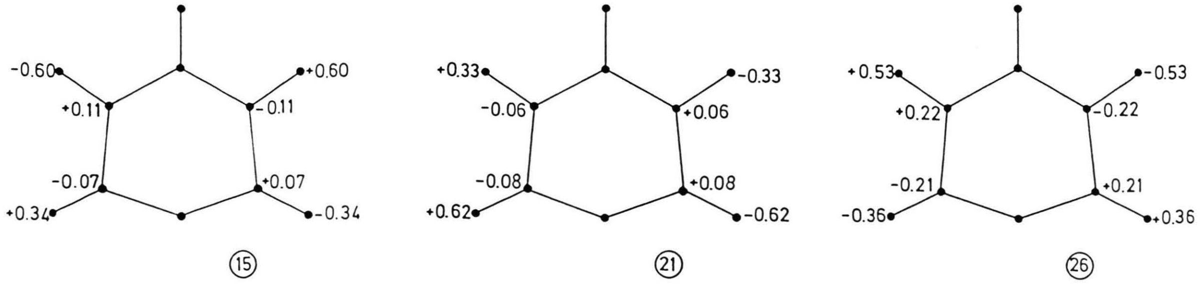


Fig. 4d. Cartesian displacement vectors (4-31G/4-31G) of A_2 symmetry (^{11}B). The numbers at the atoms correspond to the values of the y-components (cf. Figure 1). These vibrations are not active in IR. For frequencies see Table 6a.

tions 2 and 1 are the symmetric and antisymmetric stretchings of the C_2-H_7 and C_6-H_{11} bonds, respectively. Vibration 4 is mainly due to antisymmetric stretching of the C_3-H_8 and C_5-H_{10} bonds. In the symmetric normal mode (5) the C_4-H_9 bond participates significantly. Of special interest is the composite B_1 vibration 6, which, beside some $\nu(C-C)$ and $\delta(C-H)_{i.p.}$, components contains distinct stretching and shortening of the C−B bonds. Therefore, this vibration 6 is expected to exhibit a significant boron isotopic splitting, for which we calculated a value of 26.7 cm^{-1} at the 4-31G/4-31G level. Smaller but still important isotopic shifts have been calculated for the A_1 vibrations 20 (15.4 cm^{-1}) and 24 (14.3 cm^{-1}), the B_1 species 10 (16.8 cm^{-1}), and the one of B_2 symmetry 27 (9.9 cm^{-1}).

The vibrational spectra calculated by means of the MNDO method are listed in Table 6b. Again the largest $^{11}B-^{10}B$ isotopic shift is calculated for the B_1 vibration 6, which appears at 1749.6 cm^{-1} for $C_5H_5{}^{11}B$, a value which is almost identical with the 4-31G result. With 36.8 cm^{-1} the semiempirical value for the isotopic splitting is about 10 cm^{-1} larger than the *ab initio* result.

In addition we calculated the bond separation energies [19, 20] for borinine, pyridine and benzene. In the case of these three molecules the bond

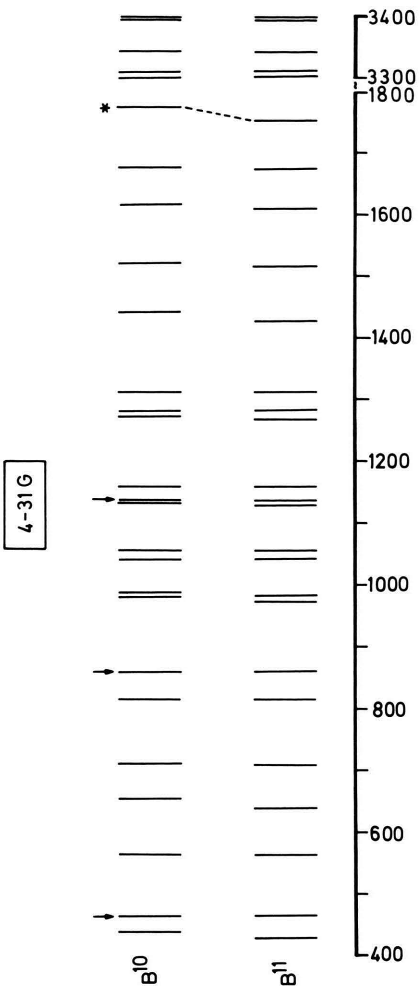


Fig. 5a. Schematic representation of the vibrational spectra of the isotopomeric borinine molecules calculated at the 4-31G/4-31G level. The star marks the B_1 vibration (6) for which the strongest isotopic shift has been calculated. The arrows indicate the A_2 vibrations, which are active in Raman only.

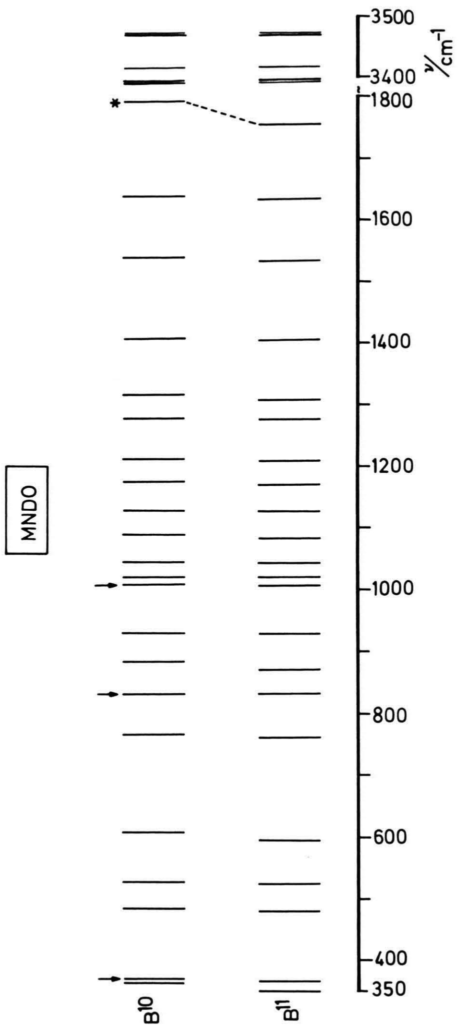
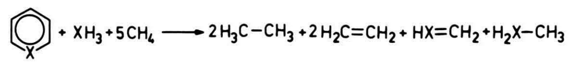


Fig. 5b. Schematic representation of the vibrational spectra of the isotopomeric borinine molecules calculated with the semiempirical MNDO method. The star marks the B_1 vibration (6) for which the strongest isotopic shift has been calculated. The arrows indicate the A_2 vibrations, which are active in Raman only.

separation reaction takes the general form:



where X=B for borinine, X=N for pyridine, and X=C−H for benzene. The total energies of the molecules used in these reactions have been taken in part from literature [21, 22]. For the remaining molecules we performed complete geometry optimizations with the STO-3G and the 4-31G basis set. All total energies, except those for borinine (see Table 1) are listed in Table 7.

The energies of bond separation are given in Table 8.

At the STO-3G level the bond separation energies are about the same for benzene and pyridine*. The value for borabenzene is about 28 kcal/mol lower.

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* See also [20], page 300 ff.

Table 7. Total energies of the molecules used in the bond separation reactions. The values for borinine are given in Table 1 (all values in a. u.).

Molecule	E_0	
	STO-3G/STO-3G	4-31G/4-31G
C_6H_6	−227.89136	−230.37776
C_6H_5N	−243.63859	−246.33132
H_3C-CH_3	−78.30618 [22]	−79.11592
$H_2C=CH_2$	−77.07396 [22]	−77.92216
$H_2C=NH$	−92.82304 [22]	−93.88258
$H_2C=BH$	−63.41037 [21]	−64.13099
H_3C-BH_2	−64.66769 [21]	−65.34843
H_3C-NH_2	−94.03286 [22]	−95.07164
BH_3	−26.07070 [21]	−26.34927
NH_3	−55.45542 [22]	−56.10669 [23]
CH_4	−39.72686 [22]	−40.13977 [23]

Table 8. Bond separation energies for borinine, pyridine, and benzene (all values in kcal/mol).

Molecule	STO-3G/ STO-3G	4-31G/ 4-31G	exp. [20]
C_6H_6	70.3*	64.1	64.2
C_5H_5N	70.3*	66.8	71.9
C_5H_5B	42.2	32.1	–

* These values might be compared with those for some main-group analogues; [20], page 375.

The energies of bond separation calculated with the 4-31G basis set are somewhat smaller. In this case the value for borinine is 32.0 kcal/mol smaller than for benzene.

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